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USE OF BY-PRODUCTS FROM THE METALLURGICAL INDUSTRY IN THE MANUFACTURE OF PROTECTIVE COMPOSITE MATERIALS

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The optimal compositions of chemically stable silicate composite materials (SCM) based on electrocorundum, which is by-product from the electrometallurgical production of niobium, are proposed. The chemical composition of electrocorundum is determined, x-ray phase and differential-thermal analyses are performed, the results of infrared spectroscopy are presented, a novel composition of electrocorundum-based ceramic paste is proposed, and the physical–chemical properties of the SCM obtained are studied. The basic characteristics of the material are: chemical stability to 99.9%, corrosion rate 0.5 – 1 mm/yr (stable), water absorption 4.4 – 5.4%, thermal stability 15 – 19, compression strength 8 – 16 MPa, shrinkage 0.1 – 0.6%, abradability 0.01 g/cm^2, and bonding strength 0.5 – 0.6 MPa.

Key words: silicate composite materials, electrocorundum, by-products from the electrometallurgical industry, semi-fireclay.

The large-scale use of wastes in the manufacture of protective materials will radically improve the environmental conditions and state of the environment in regions contaminated by wastes. It is advantageous to draw by-products of the primary production into the manufacture of composite materials, since by-products are valuable initial materials which have been subjected to preliminary mechanical and heat treatment.

The following are used to prepare composite materials which remain stable in corrosive media: pure oxides, various local clays, and production materials and wastes. The development and manufacture of new, effective, chemically stable, composite materials and protective coatings using production wastes is a very topical problem.

The production of a new generation of highly effective silicate materials requires using components with complicated chemical and mineral compositions in order to obtain high-quality composite materials for different functional purposes with improved and sometimes fundamentally new properties and a prescribed structure. The development of such materials is based on purposeful control of the technology at all its stages: use of active components, development of optimal compositions, application of chemical modifying agents, mechanochemical activation of the components, and other methods.

For the development of silicate composite materials (SCM) which hold promise for use in corrosive media, the search went no further than electrocorundum — a by-product of the electrometallurgical production of niobium — as a material with a high content of aluminum oxide, more acid-resistant and heat-conducting than other materials, and more cost-effective than conventional corundum. Its use will increase the recycling of thousands of tons of wastes produced at metallurgical plants.

The slag waste used in the present work — remelted aluminum oxide — is a valuable raw material which has been subjected to preliminary mechanical and heat treatment. It consists of a high-temperature α-phase Al_2O_3 (corundum) containing impregnations of metallic niobium particles.

Chemical analysis shows slag to contain about 1 – 4% niobium in the form of congealed drops and fine metallic inclusions. After the niobium is extracted the slag is processed — ground into powder with different particle-size fractions. The niobium impurity residues present in the acid-resistant composite material obtained impart additional corrosion resistance, since niobium possesses a number of unique physical properties.

A ceramic paste composition that includes semi-fireclay from the Lengerskoe clay deposit is proposed for obtaining acid-resistant building materials. The material can be used in

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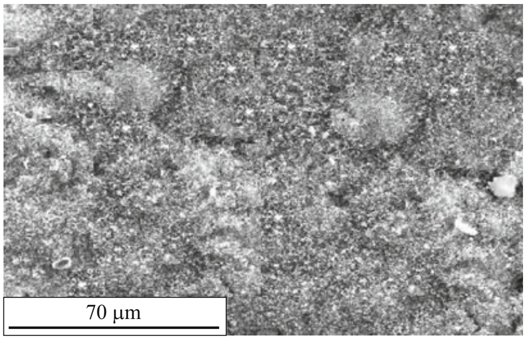

Fig. 1. Microstructure of slag with niobium particles.

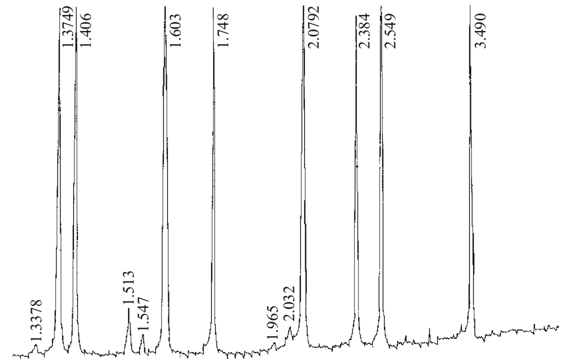

Fig. 2. Diffraction pattern of electrocorundum — slag from niobium production.

the manufacture of rapidly wearing devices and protective coatings intended for service in corrosive media at high temperatures. Semi-fireclay from the Lengerskoe deposit is widely used for making ceramic acid-resistant articles. The proposed ceramic paste considerably extends the service life of manufacturing machinery and decreases the effect of chemically active and erosion-corrosive media on them.

Liquid glass (predominately sodium) is most often used in the manufacture of acid-resistant materials and refractory coatings. It serves as a cementing base, increases the density and water impermeability of the materials, imparting to them a high quality, making them comparatively inexpensive, and allowing them to set at ordinary temperature (obtaining a mixture solidifying in air) [1]. The choice of binder — liquid glass (most widely used for setting such mixtures of water and phosphate binders) — is based on the need to make composite materials chemically stable.

In order for an irreversible reaction in which silica gel, which possesses cementing properties, precipitates from alkaline hydrosilicates to occur, chemical reagents (solidification initiators), which bind free alkali and the corresponding salts, are necessarily introduced into acid-resistant compositions. These reagents are a necessary component of liquid-glass based compositions, which without no or an inadequate amount of reagents will not possess the required stability in water at high acid-resistance. Sodium fluorosilicate in the form of a technical-grade power is usually used to initiate solidification; it was chosen as an easily obtainable solidifying agent and is also a by-product of superphosphate production.

In the course of these studies the chemical composition of electrocorundum (Table 1) was determined and x-ray phase, differential-thermal, and IR spectroscopic analyses were performed. Microscopic studies established that a considerable fraction of the niobium inclusions are smaller than 0.2 mm. X-ray phase and petrographic analyses showed that the corundum in slag corresponds in terms of grade to 23-25A electro-melted corundum with refractive indices $n_g = 1.768$ and $n_p = 1.760$ (GOST 6912–87).

The reprocessed slag consists of corundum powder. The unique physical properties of composite materials based on it determine their spheres of application — manufacturing of corrosion-resistant refractory bricks, linings, as well as putties and concretes and building material for machines used in the chemical industry [2].

X-ray phase analysis shows that diffraction peaks corresponding to interplanar distances characteristic for corundum predominate in the slag (1.3749, 1.406, 1.603, 1.748, 2.0792, 2.384, 2.549, 3.490 Å). In addition, diffraction peaks characteristic for Nb_2O_5 (1.547, 1.965, 2.032 Å) and SiO_2 (1.3378, 1.513 Å) are observed (Fig. 2).

The transformations of electrocorundum on heating were studied by differential-thermal analysis (Fig. 3). A single, weak, diffuse peak indicating an exothermal process is observed on the DTA curve. The exothermal effect in the temperature interval 470 – 680°C, which is not accompanied by mass losses in the TG curve, are probably due to the negligible phase transitions of SiO_2. This attests to the presence of a single predominant phase — corundum, which x-ray phase analysis confirms.

On the basis of its chemical composition the semi-fireclay from the Lengerskoe deposit is semisiliceous. Its heat-resistance is 1350 – 1580°C, and its Fe_2O_3 content shows that its content of coloring oxides is high. According to GOST 9169–75 the plasticity of the clay corresponds to medium plasticity (plasticity number 15.8).

TABLE 1. Chemical Composition of Electrocorundum

Base	Elements, wt.%										
Al_2O_3	Si	Fe	Mg	Mn	Cr	Pb	Cu	Zn	Ni	Co	Nb
95.3	0.85	0.12	0.7	0.01	0.02	0.04	0.57	0.02	0.001	0.001	1.00

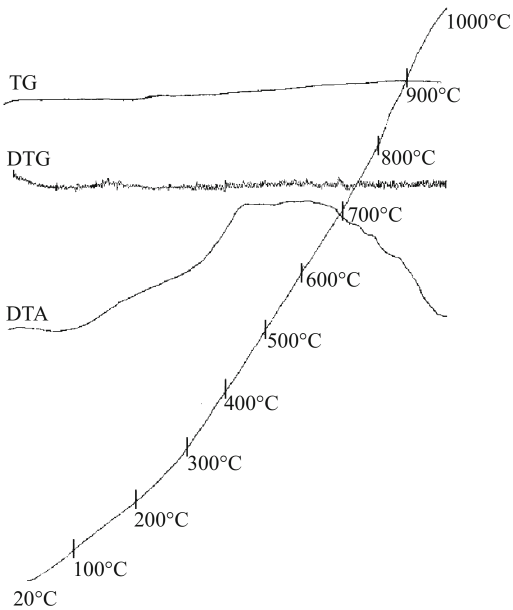

Fig. 3. DTA curve for electrocorundum — slag from the production of niobium.

Chemical composition of semi-fireclay (wt.%)

SiO_2	63.08
CaO	0.58
MgO	1.72
$Al_2O_3 + TiO_2$	22.46
Fe_2O_3 + FeO	4.5
R_2O	2.77
Other	4.89

Particle-size composition of semi-fireclay (fraction, %)

> 0.5	21.7
0.5 – 0.05	63.95
0.05 – 0.01	79
0.01 – 0.005	1 – 50.3
0.005 – 0.001	4.7 – 50.8
< 0.01	5.4 – 45.4

The prepared raw materials (slag from niobium production — electrocorundum, semi-fireclay, and sodium fluorosilicate) were weighed according to the mix composition on

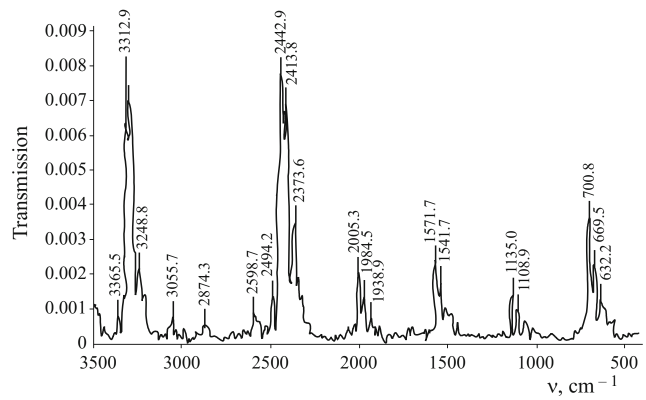

Fig. 4. IR spectra of slag from niobium production.

VLK-100 electric technical scales to within 0.001 g, loaded into a laboratory mixer, and mixed for 10 – 15 min.

The optimal compositions of the mixtures are presented in Table 2. The base of these mixes is a production by-product consisting of slag from electrothermal reduction by aluminum of niobium pentoxide — comminuted and purified fused aluminum oxide (electrocorundum) [3].

As a result of the high aluminum oxide content in slag, the acid-resistance increases. In addition, the presence of niobium oxide improves the strength properties of the final product. For niobium fluorosilicate less than 4.0 wt.% and liquid-glass content greater than 27.2 wt.%, the liquid -glass portion in the form of free alkali which has not reacted with sodium fluorosilicate lowers the material's stability in water and its strength.

For sodium fluorosilicate content greater than 4.8 wt.% and liquid-glass content less than 26.0 wt.%, excess sodium fluorosilicate is formed because the amount of liquid glass is inadequate for the reaction between sodium fluorosilicate and liquid glass to go to completion and is washed out of the system, thereby decreasing the chemical stability and strength properties of the material.

TABLE 2. Optimal Compositions of Mix Based on Electrocorundum

Sample	Content, wt.%		
	Electrocorundum*	Liquid glass	Sodium fluorosilicate
SCM-2	68.0	27.2	4.8
SCM-9	69.0	26.6	4.4
SCM-14	70.0	26.0	4.0

* Particle-size composition of electrocorundum: 0.5 – 0.4 mm — 50%; 0.2 – 0.1 mm — 50%.

TABLE 3. Optimal Compositions of Ceramic Paste

Sample	Content, wt.%			
	Electro-corundum*	Semi-fireclay	Liquid glass	Na_2SiF_6** (above 100%)
SCMcl.-1	65	5	30	5.1
SCMcl.-2	66	6	28	4.7
SCMcl.-3	67	7	26	4.4
SCMcl.-4	68	8	24	4.0
SCMcl.-5	69	9	22	3.7
SCMcl.-6	70	10	20	3.4

* Particle-size composition of electrocorundum: 0.5 – 0.4 mm — 50%; 0.2 – 0.1 mm — 50%.

** Comprises 17% of the liquid-glass mass.

TABLE 4. Test Results for Optimal Samples in Chemical Solutions

Sample	$H_2SO_{4(concentr.)}$		HCl (35%)		NaOH (35%)	
	Chemical stability	Corrosion rate, mm/yr	Chemical stability	Corrosion rate, mm/yr	Chemical stability	Corrosion rate, mm/yr
SCM-2	94.9	1.0	95.7	0.8	96.0	0.7
SCM-9	97.3	0.6	96.1	0.7	97.8	0.6
SCM-14	99.9	0.5	99.7	0.5	99.0	0.5
SCMcl.-1	96.0	0.7	96.8	0.6	96.7	0.6
SCMcl.-2	96.0	0.7	97.0	0.6	97.2	0.6
SCMcl.-3	96.8	0.6	97.2	0.6	96.9	0.6
SCMcl.-4	97.3	0.6	98.6	0.5	98.6	0.5
SCMcl.-5	97.7	0.6	98.5	0.5	98.2	0.5
SCMcl.-6	98.9	0.5	98.7	0.5	98.5	0.5
SCM-14	99.9	0.5	99.7	0.5	99.0	0.5

The recommended amounts of sodium fluorosilicate and liquid glass for electrocorundum, which is a slag from niobium production, is optimal for obtaining acid-resistant and strong composite lining material which is stable in water (see Table 2).

Table 3 gives the optimal compositions of ceramic paste, which contains semi-fireclay, slag from industrial production, liquid glass, and sodium fluorosilicate, in the following component ratios (wt.%): 20 – 30%, semi-fireclay (fractions no larger than 0.5 mm) — 5 – 10%, electrocorundum (fractions no larger than 1 mm) — 65 – 70%, sodium fluorosilicate — 3.4 – 5.1% [4]. A ceramic paste with the content of electrocorundum, semi-fireclay, liquid glass, and sodium fluorosilicate (introduced to accelerate solidification) in precisely these proportions makes it possible to obtain with kilning at 1100°C a material with high strength, heat-resistance, and chemical stability (in sulfuric and hydrochloric acids and in alkali solutions) and low water absorption.

For electrocorundum content higher than 70%, semi-fireclay content higher than 10%, and liquid-glass content higher than 30%, the open porosity, water-absorption, and gas permeability all increase, the chemical stability decreases, and the articles lose their strength properties.

Using less than 65% electrocorundum, less than 5% semi-fireclay, and less than 20% liquid glass is inadequate to obtain ceramic material (coating) with high strength properties, chemical stability, low water absorption, and gas permeability.

When the mix components are introduced in the indicated proportions and with the appropriate particle-size composition, conditions are created for obtaining a uniform plastic paste and tight filling of space a protective coating is deposited.

The corrosion rate of the optimal samples of the composite materials was determined in sulfuric and hydrochloric acids as well as in alkali at room temperature for sintered samples in the form of rectangular bars with a ground surface. The specific mass losses of the samples in the course of the tests were 2.30 – 2.88 $g/(m^2 \cdot h)$. Table 4 gives the corrosion rates of SCM (0.5 – 1 mm/yr), which on the scale for evaluating the corrosion resistance of silicate materials corresponds to a “stable” assessment. Table 5 gives the basic physical-technical properties of the optimal SCM samples [5].

The following conclusions can be drawn from this work:

– new protective materials based on technogenic wastes have been developed;

– the SCM obtained are characterized by chemical stability (in concentrated sulfuric acid — from 89.6 to 99.0%, in hydrochloric acid — from 88.7 to 99.7%, alkali-resistance — from 81.7 to 99.0%); mechanical strength (erosion-abrasion resistant); water absorption conforming to the norm;

TABLE 5. Properties of Samples without Heat Treatment and Kilned at 1100°C

Sample	Air shrinkage, %	Density in air-dry state, g/cm^3	Apparent porosity, %	Density, g/cm^3	Abradability, g/cm^2	Bonding strength,* MPa	Water absorption, %	Thermal conductivity, $W/(m \cdot K)$	Thermal stability, number of temperature changes 800°C – water (5 – 25°C)		Strength, MPa	
									before crack appearance	before fracture	compression	bending
SCM-2	0.1	1.56	7.0	2.9	0.01	0.5	4.3	6.4	15	21	75.2	9.7
SCM-9	0.1	1.52	7.1	2.8	0.01	0.6	5.2	6.6	15	20	80.7	11.7
SCM-14	0.1	1.51	7.2	2.8	0.01	0.5	5.4	6.7	15	21	81.2	13.2
SCMcl.-1	0.3	1.45	6.9	3.0	0.03	0.5	5.0	6.9	18	22	102	14
SCMcl.-2	0.3	1.41	6.9	3.1	0.02	0.5	5.3	6.8	19	23	102	14
SCMcl.-3	0.4	1.41	7.0	3.1	0.02	0.5	4.5	6.9	17	22	104	14
SCMcl.-4	0.4	1.45	7.0	3.1	0.01	0.5	5.2	6.9	18	22	105	15
SCMcl.-5	0.5	1.47	6.9	3.2	0.01	0.5	5.0	6.9	19	24	110	16
SCMcl.-6	0.6	1.60	6.9	3.2	0.01	0.5	4.5	6.9	19	24	110	16

* Paste without heat treatment.

– electrocorundum in large amounts (> 65 wt.%) is a structure-forming element of SCM, determining the thermal and physical-mechanical properties;

– liquid glass in large amounts (to 30%), being a cementing base of the mix, participates in the formation of the crystal glass structure of the ceramic material, containing semi-fireclay from the Lengerskoe deposit, during heat treatment of the ceramic (to 1100°C).

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